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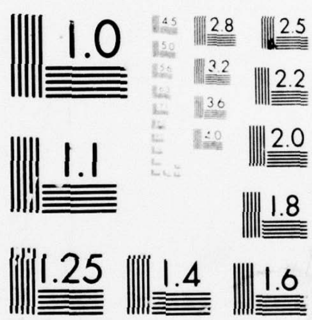

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Contract N00014-76-C-0020 new NR032-544

FINAL REPORT

1) CREEP AND RELAXATION BEHAVIOR OF VAPOR-DEPOSITED AMORPHOUS SELENIUM FILMS: 2) FLOW BEHAVIOR OF GLASSY METALS

By

David Turnbull

December 1976

Division of Engineering and Applied Physics
Harvard University, Cambridge, Massachusetts

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

It has been shown that a-Se films deposited from the vapor onto low temperature substrates, when annealed at or just below their glass temperature, become indistinguishable, in flow and transformation behavior, from melt-quenched specimens. Photoillumination, in the visible range, of these films (a) sharply increases their rate of approach to configurational equilibrium while not affecting the flow rate of equilibrium, (b) greatly increases the number density of crystals heterogeneously nucleated while not producing

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measurable homogeneous nucleation, (c) generally increases the rates of growth of crystals within the films.

It has been shown that the plastic deformation behavior of glassy metals can be represented satisfactorily by a deformation map of the type presented by Ashby and Frost for various crystalline materials. The available evidence indicates that the temperature dependence of the isoconfigurational creep rate below the glass temperature is relatively much smaller for metallic alloy than for non-metallic glasses.

END OF THE YEAR REPORT: ONR CONTRACT N00014-76-C-0020

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1. Creep and Relaxation Behavior of Vapor-Deposited Amorphous Selenium Films.

R.B. Stephens of our laboratory (paper in preparation) developed a high precision technique for measuring the creep rates of thin films. With this technique he investigated the dependence of the creep rates of a-Se films, when relaxing toward configurational equilibrium and when in their fully relaxed states, on time, temperature and photoillumination. The following conclusions emerged from this study.

a) The shear viscosities of the fully relaxed vapor-deposited films are practically identical with those of bulk melt-quenched specimens, measured [by Jenckel, Kolloid Zeit 84, 266 (1933) and by Cukierman and Uhlmann, J. Non-Cryst. Solids 12, 199 (1973)], by quite different methods, over the entire viscosity range, 10^{10} to 10^{12} poise, of measurement overlap. Stephens' measurements extended beyond the overlap range to the viscosity 3×10^{14} poise.

b) From the relaxation studies, the temperature dependence of the isoconfigurational flow of the films in various, partly relaxed states was determined. The activation energy, E_J, opposing this flow was about 50 kcal/gm.atom, roughly independent of the degree of relaxation. This value is, roughly, only 40% of the apparent activation energy, $E_\eta \sim 130$ kcal/gm.atom, for flow in the fully relaxed state.

c) Illumination with light in the visible range had no measurable effect on the creep rates of the fully relaxed specimens but it sharply increased the relaxation rates toward configurational equilibrium.

d) The far infrared spectrum of fully relaxed films is virtually indistinguishable from that of melt-quenched specimens.

e) Thus, despite the rather large energy barrier thought to oppose ring-chain interconversion in a-Se, films of a-Se relax quite rapidly in the glass transition range to configurational states which appear to be the same as those of bulk melt-quenched specimens.

2. Flow Behavior of Glassy Metals.

Our analysis indicates that, just as for a-Se, the rate constant for homogeneous creep of any glassy metal is composed of an isoconfigurational mobility factor and a configurational excitation factor determined by the actual average configuration (e.g., as characterized by the free volume or configurational entropy). Further the available data on the homogeneous creep rates of glassy metals, at temperatures near to and far below the glass temperature, yield activation energies, E_J, for isoconfigurational flow which, in contrast with the results on a-Se, are only a small fraction, $\lesssim \frac{1}{10}$, of the apparent activation energy for flow in the fully relaxed states. An important consequence of this behavior is that high flow rates can persist in localized regions where high amounts of configurational disorder are retained or imposed by some external force to temperatures far below the glass temperature.

Spaepen showed (ONR Technical Report No. 7, "A Microscopic Mechanism for Steady State Inhomogeneous Flow in Metallic Glasses") that the available deformation data on glassy metals can be satisfactorily represented by a deformation map of the type presented by Ashby and Frost for various crystalline materials. This map depicts creep rates and the prevailing deformation mechanism with variances of the reduced temperatures and flow stresses. The position of the boundary line between the homogeneous and inhomogeneous flow regions on the deformation map was consistent with calculations of it based on the concepts outlined above and the free volume model for flow.

Papers Published or in Press

1. Frans Spaepen and R.B. Meyer, "The Surface Tension in a Structural Model for the Solid-Liquid Interface", Scripta Met. 10, 257 (1976).

2. R.B. Stephens, "Relaxation Effects in Glassy Selenium", J. Non-Cryst. Solids 20, 75 (1976). Also ONR Technical Rept. #3, N00014-67-A-0298-0036, NR-032-544 (February 1975).

3. M. Marcus and D. Turnbull, "On the Correlation between Glass Forming Tendency and Liquidus Temperature in Metallic Alloys", Mats. Sci. and Eng. 23, 211 (1976). [Paper presented at Second International Conference on Rapidly Quenched Metals (M.I.T.)].

4. Frans Spaepen, "A Microscopic Mechanism for Steady State Inhomogeneous Flow in Metallic Glasses", ONR Technical Report No. 7, N00014-67-A-0298-0036, NR-032-544 (August 1976).

5. G. Gross, R.B. Stephens and D. Turnbull, "On the Crystallization of Amorphous Selenium Films: Thermal and Photo Effects", J. Appl. Phys. 48, 1139 (1977).

6. F. Spaepen and D. Turnbull, "Formation of Metallic Glasses", invited paper in Second International Conference on Rapidly Quenched Metals, Nov. 1975, M.I.T.; in press, Conference Proceedings.

7. F. Spaepen and D. Turnbull, "Transport and Transformation Behavior in Metallic Glasses", invited paper at A.S.M. Seminar on Amorphous Metals, Sept. 1976, Niagara Falls, N.Y. To appear as ONR Technical Report No. 1, N00014-76-C-0020, NR-032-544, and in press, Conference Proceedings.

8. D. Turnbull, "Formation and Transformation Behavior of Amorphous Solids", in Physics of Structurally Disordered Solids (edited by S.S. Mitra), pp. 1-7, Plenum Press (1976).

Technical Report and Paper in Preparation.

1. R.B. Stephens, "The Viscosity and Structural Relaxation Rate of Amorphous Selenium" , submitted to J. Appl. Phys.

David Turnbull: Invited Talks 1976

1. New York Academy of Sciences Workshop on the Glass Transition and Nature of the Glassy State, "Relation of Crystallization Behavior to Structure in Amorphous Systems", Dec. 1975.

2. Northeastern University Chemistry Department Colloquium, "The Glass Transition in Monatomic Systems", 1/19/76.

3. Ohio State Metallurgy and Ceramics Seminar, "Models for the Crystal-Melt Interfacial Tension and Implications to Solidification", 5/28/76.

4. International Magnetism Conference, Pittsburgh: "Formation and Stability of Amorphous Ferromagnetic Alloys", 6/18-76.

5. La Jolla Materials (ARPA) Council: "Metallic Glasses: Genesis and Structure", 7/19/76.

6. Gordon Conference on Physical Metallurgy, "Thermodynamic and Kinetic Factors in Glass Formation", 7/12/76.

7. Second International Symposium on Amorphous Ferromagnetism, R.P.I., Troy, N.Y., "Atomic Transport and Transformation Behavior of Glassy Metals", 8/27/76.

8. A.S.M. Seminar on Metallic Glasses, Niagara Falls, N.Y.: "Atomic Transport and Transformation Behavior of Glassy Metals", 9/18/76.

9. Corning Glass Research Laboratory Colloquium: "Formation, Structure and Properties of Glassy Metals", 10/22/76.

Frans Spaepen: Invited Talks 1976

1. Gordon Research Conference on Physical Metallurgy: "Models for Flow and Fracture of Amorphous Metals", 7/14/76.

2. Colloquium on "Liquid Metals and the Solid-Liquid Interface", Carry-Le-Rouet, France: "Configurational and Entropic Aspects of the Solid-Liquid Interface", 11/18/76.

3. 10th Metals Conference - "Physical Properties of Amorphous Metals", Utrecht, the Netherlands: "Flow and Fracture of Glassy Metals", 11/23/76.

Other Contracts

1. "Study of the Mechanisms for "Fast Diffusion in Metals". National Science Foundation.

2. Share of Materials Research Laboratory, National Science Foundation.

3. Adviser (no student or post-doctoral report) on "Preparation and Characterization of Improved Superconducting Materials". National Science Foundation.